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Detached growth of gallium doped germanium

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Abstract

Detached Bridgman growth of gallium-doped germanium itself as well as the transition from detached to attached growth was observed in-situ for the first time, using a quartz-glass ampoule in a mirror furnace. Crystal diameter was 9 mm, the growth length 41 mm, and the growth velocity 0.5 mm/min. Undoped 1 1 1-oriented germanium served as seed material; the melt was doped with gallium ($C_0 = 8.2 \times 10^{18}$ at/cm^3). Detachment took place after a growth length of 7 mm and continued for 27 mm; the remaining 7 mm grew with wall contact again. The wall-free growth could be observed around the entire circumference except for some small bridges (width: a few tens of micrometers, length: some hundreds of micrometers), where the crystal grew in contact with the wall. In the detached-grown part of the crystal, the 1 1 1-related growth lines are clearly visible. The transition from attached to detached growth and vice versa did not take place along a straight line but transitioned as islands over a length of about 1 mm. The gap between the growing crystal and the container wall varied between 10 and 80 μm, as measured by a profilometer. The etch pit density is greatly reduced in the part of the crystal that grew free of the wall. An increase in the EPD is seen in the area where the crystal had contact with the ampoule wall by the bridges described above. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The first reports of detached growth (also called de-wetting or necking) are already more than 20 years old; they are some of the results of the Skylab missions (e.g., Yue and Voltmer with germanium in a graphite-crucible [1], or Witt et al. with InSb in quartz glass ampoules [2,3]). In the intervening years, detached Bridgman growth has been observed in many μg-experiments; an excellent overview about the substances and the crucible materials is given by Wilcox and Regel [4,5] and by Duffar et al. [6]. One of the most recent results was presented by Larson et al. [7–9]: extensive characterization of partially detached grown CdTe crystals (USML-1 and -2 missions) regarding dislocation density, grain structure, transmittance, stress etc., demonstrating the positive influence of detachment on the quality of the grown crystals.

Although the mechanism of detached growth is not yet clear in all details, there is a common understanding about the main factors playing an

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important role for the appearance of detached growth:

- high contact angle between the melt and the crucible material/poor wetting of the crucible by the melt,
- high growth angles,
- gas pressure in the ampoule/pressure difference between the gap and the head of the melt,
- reduced hydrostatic pressure.

Duffar et al. [10–13] pointed out that rough crucibles support de-wetting or at least reduce the melt area which is in contact with the crucible and lead therefore to reduced melt contamination, but the remaining ridges can give rise to secondary nucleation, twins, and grains.

According to Wilcox and Regel [14–18], detachment is supported or even initiated by the gas pressure due to the rejection of volatile impurities at the solid–liquid interface and liberation of these impurities through the meniscus into the gap between crystal and ampoule.

A common feature of nearly all the growth processes where detachment was observed, was the fact that the experiments were performed under microgravity: under normal gravity, the liquid might be pressed into the gap between crystal and crucible due to the hydrostatic pressure and the shape of the meniscus is influenced in an undesirable way. A second point is that convective mixing of the melt under 1 g conditions prevents the accumulation and evaporation of the rejected gas at the solid–liquid interface [4,18]. Another possibility to overcome the hydrostatic pressure was recently demonstrated by Duffar et al. [19]: detachment of GaSb was forced by active pressure control between the separated gas volumes at the top and the bottom of the melt.

The unanimous result of all detached grown crystals is the improved crystal quality in the parts which grew without wall contact, see e.g. Refs. [4,8,10,20,21]. According to these results, the main benefits are:

- less contamination of the melt by the crucible material;
- stress caused by different thermal expansion coefficients (crystal/crucible) is reduced, leading to fewer dislocations and point defects;
- reduced nucleation of grains and twins at the ampoule wall.

None of the crystals showed indications of thermocapillary mixing due to the free surface of the meniscus (see literature review in Ref. [6]) or at least no signs of time-dependent Marangoni convection has been found.

Most of the experiments reported in the literature have been performed either in resistance furnaces, in coated ampoules (Duffar [22] used a mirror furnace but a gold coated quartz ampoule), or in non-transparent crucible material (BN, graphite). Therefore little has been observed regarding the interaction of melt, crucible, and crystal. Wilcox et al. [4] investigated the wetting behavior of Hg in transparent ampoules and of InSb in a transparent furnace and observed that the melt did not lose contact with the wall.

An interesting fact was shown by Duffar et al.: the contact angle between melt and crucible is very sensitive to the surface condition and the treatment of material. In particular cases a contact angle as high as 170° was measured for InSb on silica instead of 112° [21]. This was attributed to absorption of impurities at the surface of the melt.

For semiconductor melts, the contact angles versus typical crucible materials such as SiO_2, C, or pBN are in the range of 100–150° [23–25]. Most of the melts show the highest contact angle against pBN, they are in general about 10–20° larger than for silica.

Recently performed sessile-drop measurements for germanium on different substrates and various gas atmospheres confirmed these values [26]; a contact angle as high as 170° was observed for Ge on pBN, but only 117–150° for silica, depending on the surface treatment and the atmosphere. Further, it was observed that the absolute value is very sensitive to impurities and reaction between melt and substrate.

2. Experimental setup

2.1. Ampoule preparation and growth facility

The crystal was grown in a double-wall quartz-glass ampoule; a sketch of the arrangement is shown in Fig. 1. The diameter of the seed and the growing crystal were 9 mm, the length of the seed 35 mm and the length of the grown crystal was 41 mm. Before the starting material was loaded into the ampoule, the quartz was cleaned with MUCASOL™ and H_2O (18 MΩ) and baked out under vacuum (10^{-6} mbar) at 1100°C for 2 h. Undoped germanium (1 1 1-oriented) served as the seed, the feed was pill-doped with gallium resulting in an average concentration of $C_0 = 8.2 \times 10^{18}$ at/cm^3. First, the germanium was rinsed with H_2O (18 MΩ) followed by acetone. Than it was etched for about 3 min with the 18 : 8 : 5 polishing etch ($HNO_3 : CH_3COOH : HF$) [27]. After this treatment, the germanium shows a smooth and shiny surface. The material was than loaded into the ampoule and baked out at 900°C for 2 h under alternating atmospheres of H_2 (normal pressure) and vacuum (10^{-6} mbar). Finally, the ampoule was sealed under an argon pressure of 600 mbar (pressure at room temperature).

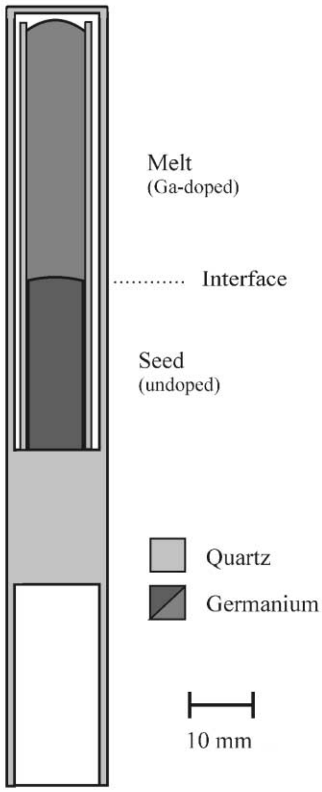

Fig. 1. Sketch of the growth ampoule.

The growth experiment took place in a mono-ellipsoid mirror furnace [28]. To obtain a temperature profile suited for Bridgman growth, the lamp was moved 2 mm out of focus toward the center of the furnace. A detailed description of this arrangement as well as the resulting axial temperature profile is given in Ref. [28]. The solid–liquid interface was observed by a borescope placed outside of the furnace. It is connected to a video tape recorder via a lens system and a CCD camera. The optical window through the mirror furnace wall consists of a quartz glass plate (diameter: 6 mm).

The advantage of this setup is the optical access and the possibility to observe and record the position of the growing interface. The drawback is the restricted growth length of approximately 40–45 mm and the steep temperature gradient of about 100 K/cm at the interface and within the grown crystal, increasing the development of stress and dislocations.

The ampoule was heated up within 15 min and kept at a constant temperature for 45 min to guarantee a homogeneous distribution of the dopant in the melt. For the growth process, the ampoule was pulled down with a constant velocity of 0.5 mm/min. No ampoule rotation was applied.

2.2. Crystal preparation and characterization

The surface of the grown crystal was analyzed by scanning electron microscopy (SEM) and by profilometer measurements. The sample was first cut axially (parallel to the 1 1 0-plane) for segregation measurements (4-point probe measurements and analyses by Nomarski Differential Interference Contrast Microscopy-NDIC). The axial slab was polished with 9 and 1 μm diamond paste and SYTON™ and etched with the 1 1 1-etch ($H_2O_2 : CH_3COOH : HF$) for 30 s. From the remaining part of a half cylinder, radial wafers were cut (orientation: ⟨1 1 1⟩, thickness: 3 mm), polished and etched by the Billig etch (12 g KOH, 8 g $K_3[Fe(CN)_6]$, dissolved in 100 ml H_2O) for 8 min at ≈80°C [29] to reveal the etch pit density distribution.

3. Results

After growing ≈7 mm by the normal Bridgman mode with wall contact, detachment started and continued for 27 mm. The wall-free growth took place around the whole circumference of the crystal except for some small bridges. (This topic will be discussed in more detail later on corresponding pictures are shown in Fig. 6 as part of the discussion of the etch pit density.) In the detached grown part, the three 1 1 1-related growth lines (or micro-facets) could be seen, one of them is shown in Fig. 2 on the left-hand side. The remaining 7 mm of the crystal grew again with wall contact. The transition from detached to attached growth is also seen in Fig. 2. In a video tape, the demarcation line, where the transition from de-wetting to wetting behavior occurred, was visible in the melt region as soon as that line came into view. This suggests that the detachment is mainly influenced by the surface condition of the container wall. This hypothesis is strengthened by the fact that the transition is not a straight line but somewhat irregular. That is, in some areas the crystal was already growing with wall contact at the same time that other areas were still growing free of the wall.

With the transition from detached to attached growth, there is a related increase of the crystal diameter (see Figs. 3 and 4). Measuring the height profile of the grown crystal using a profilometer, the gap width (i.e. the distance between the crystal and the container wall) has been determined. The gap varies between 10 and 80 μm, with small areas where the crystal touched the ampoule wall (Fig. 3, see also Fig. 6, left-hand side). It can be concluded that the size of the meniscus has not exceeded some tens of micrometers, and the thermocapillary convection which can arise from such a small free surface area can be neglected or is at least not in the time-dependent state. This is in agreement with the literature [6]. The absence of time-dependent convection has been proven by the lack of dopant striations in the detached grown part (Fig. 4). It shows a NDIC-image of the etched axial crystal: the lower part was grown without wall contact, the upper part with wall contact. Only some etch pits are visible. Due to the absence of dopant striations, the interface curvature can be determined only at the transition between the undoped

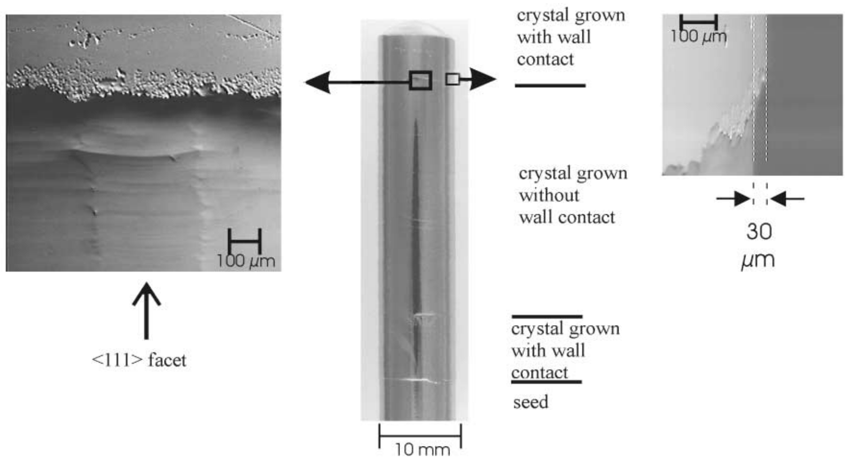

Fig. 2. Photograph of the complete crystal (middle part) and SEM-images of the surface, showing the transition from detached to attached growth. Front view on the left, side view on the right-hand side.

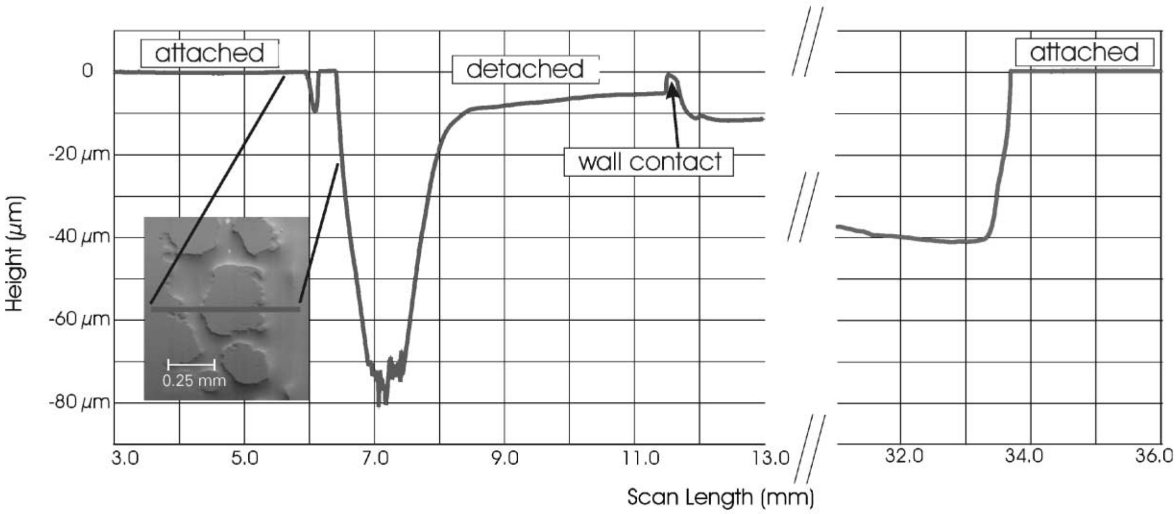

Fig. 3. Axial height profile of the crystal: the gap between the crystal and the container wall was approximately 10–80 µm wide, interrupted only by some small bridges.

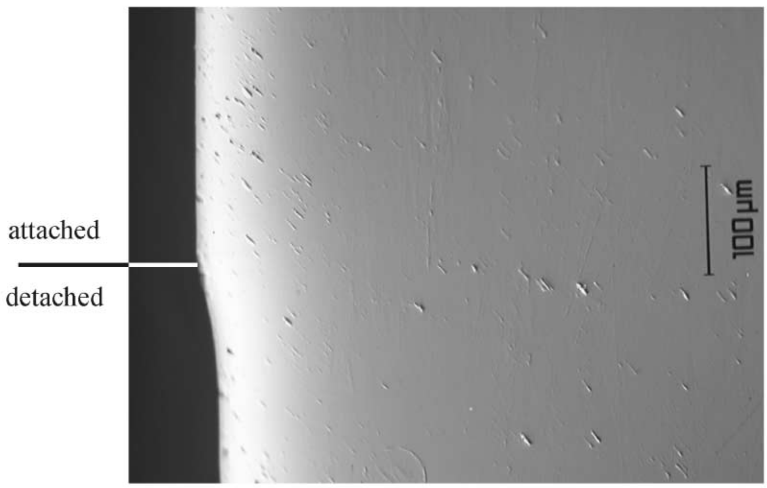

Fig. 4. Micrograph of the etched crystal slab at the transition from detached to attached growth: no microsegragtion is induced by the detached growth.

seed and the doped crystal. The phase boundary is slightly convex with a deflection toward the melt of approximately 250 µm.

The axial macrosegregation was measured with a 4-point probe. The dopant distribution (Fig. 5) lays between the theoretical curves for complete mixing (Scheil equation [30]) and purely diffusive mass transport (Tiller equation [31]). For the calculation, $k_0 = 0.087$ and $D = 1.9 \times 10^{-4}\,\text{cm}^2/\text{s}$ were used [32]. The reduced mixing indicates low radial temperature gradients and a rather flat solid–liquid interface. At the transition attached/detached ($x = 7\,\text{mm}$) as well as at the reverse transition ($x = 34\,\text{mm}$),

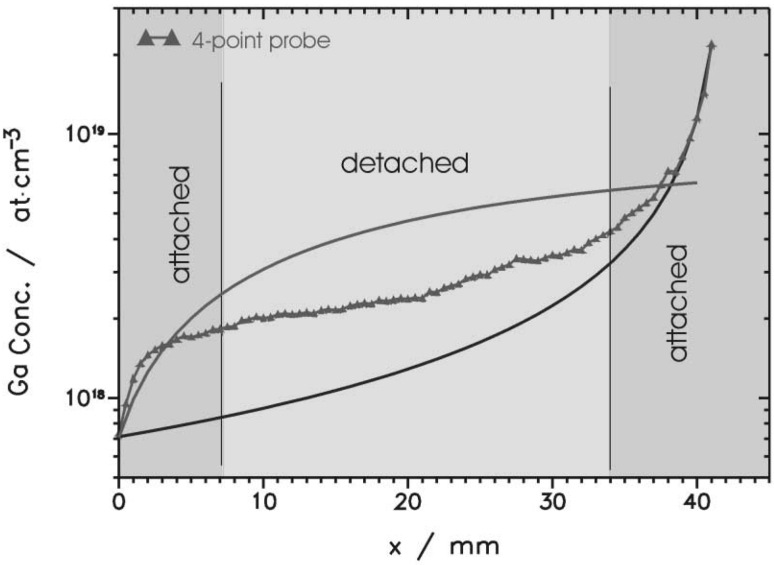

Fig. 5. Axial dopant distribution, measured by 4-point probe. The detachment does not influence the macrosegregation.

no influence of the melt–ampoule interaction on the macrosegregation (i.e. on the mixing state of the melt) is seen.

As mentioned above, the crystal grew detached except for several small bridges, where the melt was in contact with the ampoule wall (Fig. 6, left-hand side). The dimension of these bridges is several tens of micrometers in width and some hundreds of micrometers in length. A similar observation was made by Witt et al. [2,4] (and described as "Chinese wall"). This implies that the surface layer which prevented wetting of the quartz wall by the melt was not coating the ampoule entirely but was disconnected at some points. Looking at the radial EPD-distribution (Fig. 6), these bridges are related to a strong increase of the defect structure. Due to the high temperature gradient during the growth process and an EPD of $>10^4$ in the seed material, the overall EPD in the grown crystal is high. But a clear tendency is seen comparing the parts grown with contact and without wall contact. In the detached areas close to the wall, the EPD is less by more than one order of magnitude compared to attached areas (areas near the bridges).

4. Discussion

Without taking into account the hydrostatic pressure, the sum of the growth angle α of the crystal and the contact angle θ of the melt (with respect to the container wall) has to be larger than or equal to 180° to realize detachment [21,33]. Looking at the values for α and θ given in literature (growth angle: $\alpha_{\mathrm{Ge}} = 7 - 12^\circ$ [21]; wetting angle for a germanium melt on silica: $\theta_{\mathrm{Ge}} = 106^\circ$ [6] or 116–150° [26], respectively), this is normally not the case. Even if $\alpha + \theta \geqslant 180^\circ$ is not satisfied (with θ = contact angle of the melt toward the "normal" container wall), detached growth can be initiated or maintained by a favorable combination of surface treatment (or the coating or the status of oxidation [34]) of the container [21] and the gas pressure at the triple point (melt-crystal-container) compared to the pressure above the melt [15]. Applying the relation introduced by Duffar et al. [21]

$$\varepsilon = r((\cos\alpha + \cos\theta)/\cos\theta),$$

where ε stands for the gap-width between crystal and ampoule wall, r is the radius of the crystal, α is

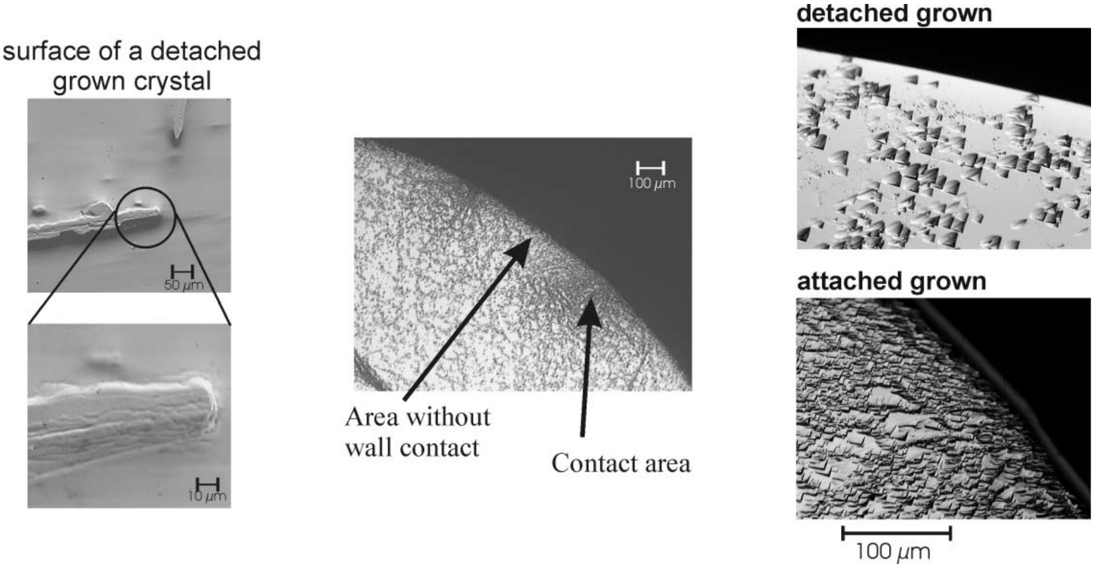

Fig. 6. Small bridges where the crystal had contact to the ampoule wall (left-hand side) caused a great increase in the EPD (right-hand side).

the growth angle and θ the contact angle, a contact angle of $174 \pm 4^\circ$ is needed to obtain a gap width of about 30 μm. This relation does not consider a gas pressure difference between the meniscus and the top of the melt, a condition which was realized in our configuration because there was gas exchange between the location of the meniscus and the top of the ampoule. The transitions from attached to detached growth and vice versa, as well as the irregular transition (i.e. the simultaneous appearance of attached and detached growth at different positions of the interface), suggest that the surface condition of the quartz glass ampoule was the main source for the detachment in this case. The exact mechanism of the different wetting behavior cannot be explained yet and will be the subject of systematic investigations (e.g. measurement of the contact angle with respect to surface treatment of the quartz glass).

An important point is that detached growth is possible even under normal gravity conditions where the hydrostatic pressure tends to force the melt to fill any gap between the crystal and the container wall.

5. Summary

For the first time, detached Bridgman growth of gallium doped germanium was observed in situ. The main results can be summarized as follows:

- The gap between the detached-grown crystal and the wall of the quartz-glass ampoule was measured to be in the range of 10–80 μm.
- Detached growth occurred around the whole circumference of the crystal; the crystal was in contact with the ampoule only at some small bridges.
- The transition from attached to detached and vice versa did not take place along a straight line but was irregular within a region of about 1 mm.
- No dopant striations are seen in NDIC-images, indicating that the free surface of the melt meniscus does not cause time-dependent thermocapillary convection.
- No influence of the detachment is seen on the macrosegregation. The axial dopant distribution lays between the theoretical curves for complete mixing and diffusive mass transport.

- In the areas close to the wall, the EPD is reduced by more than one order of magnitude for crystal parts grown detached compared to those grown attached.

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